

A comparison between algebraic models of molecular spectroscopy

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Abstract

We discuss a symmetry-adapted algebraic (or vibron) model for molecular spectroscopy. The model is formulated in terms of tensor operators under the molecular point group. In this way, we have identified interactions that are absent in previous versions of the vibron model, in which the Hamiltonian is expressed in terms of Casimir operators and their products. The inclusion of these new interactions leads to reliable spectroscopic predictions. As an example we study the vibrational excitations of the methane molecule, and compare our results with those obtained in other algebraic models.

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1 Introduction

The development and refinement of experimental techniques in high resolution spectroscopy has generated a wealth of new data on rovibrational spectra of polyatomic molecules. Highly symmetric molecules, such as tetrahedral XY_4 systems, form an ideal testing ground. On the one hand, the high degree of symmetry tends to reduce the complexity of the spectrum and on the other hand, the use of symmetry concepts and group theoretical techniques may help to interpret the data and eventually suggest new experiments [1, 2]. A good example is provided by the methane molecule, for which there exists a large amount of information on vibrational energies.

Ab initio calculations for rovibrational spectra of molecular systems attempt exact solutions of the Schrödinger equation. These calculations involve several configurations associated with the molecular electronic states and yield the force field constants [3, 4] from which the spectrum can be generated [5]. For small molecules this procedure is still feasible, but this is in general not the case for polyatomic molecules, due to the large size of the configuration space. Despite the progress made in *ab initio* calculations, a direct comparison with experimental vibrational energies of methane still shows large deviations, especially for vibrational states with a higher number of quanta.

An alternative method is provided by algebraic (or vibron) models (for a review see [6, 7]). The general method consists of two ingredients: (i) the introduction of $U(k+1)$ as the spectrum generating algebra for k degrees of freedom, and (ii) for a system of bosonic degrees of freedom the states are assigned to the symmetric representation $[N]$ of $U(k+1)$.

In its original formulation [8, 9], rotations and vibrations were treated simultaneously in terms of coupled $U(4)$ algebras: $\mathcal{G} = U_1(4) \otimes U_2(4) \otimes \dots$, by introducing a $U(4)$ algebra for each bond ($k = 3$). The electronic degrees of freedom can be included by introducing a unitary group for the electrons [10]. For polyatomic molecules it was found to be more convenient to first separate the rotations and vibrations and subsequently to treat the vibrations in terms of coupled $U(2)$ algebras [11, 12]: $\mathcal{G} = U_1(2) \otimes U_2(2) \otimes \dots$, introducing a $U(2)$ algebra for each interatomic potential ($k = 1$). In this version of the vibron model the calculation of matrix elements is greatly simplified. An additional advantage is that it is well-suited to incorporate the underlying discrete symmetries.

In a different approach, it has been suggested to use a $U(k+1)$ model for the $k = 3n - 3$ rotational and vibrational degrees of freedom of a n -atomic molecule [13]. This model has the advantage that it incorporates all rotations and vibrations and takes into account the relevant point group symmetry. However, for larger molecules the number of possible interactions and the size of the Hamiltonian matrices increase rapidly. A similar approach can be used for the vibrations only [14].

In this contribution, we discuss a symmetry-adapted version of the vibron model [15, 16, 17, 18] which is very well suited to describe the vibrations of polyatomic molecules, especially those with a high degree

of symmetry. The method is based on a set of coupled $U(2)$ algebras, whose generators are projected on tensor operators under the molecular point group. In order to illustrate these ideas we first review the main ingredients of the $U(2)$ vibron model, its connection with the Morse oscillator and the harmonic limit. Next we develop the formalism in more detail and take as an example the methane molecule which has tetrahedral symmetry. Wherever possible, we make a comparison between the present formulation and other algebraic models.

2 The $U(2)$ vibron model

The model is based on the isomorphism of the $U(2)$ Lie algebra and the one-dimensional Morse oscillator, whose eigenstates can be associated with $U(2) \supset SO(2)$ states $[[N], m\rangle$ [19]. The $U(2) \supset SO(2)$ algebra is generated by the set $\{\hat{G}\} \equiv \{\hat{N}, \hat{J}_+, \hat{J}_-, \hat{J}_0\}$, which satisfies the commutation relations

$$[\hat{J}_0, \hat{J}_\pm] = \pm \hat{J}_\pm, \quad [\hat{J}_+, \hat{J}_-] = 2\hat{J}_0, \quad [\hat{N}, \hat{J}_\mu] = 0, \quad (1)$$

with $\mu = \pm, 0$. For the symmetric irreducible representation $[N]$ of $U(2)$, the Casimir operator is given by $\vec{J}^2 = \hat{N}(\hat{N} + 2)/4$, from which follows the identification $j = N/2$. The $SO(2)$ label is denoted by m . The Hamiltonian

$$\hat{H}_M = \frac{A}{2} (\hat{J}_- \hat{J}_+ + \hat{J}_+ \hat{J}_-) = A (\vec{J}^2 - \hat{J}_0^2). \quad (2)$$

corresponds to the Morse oscillator with energies

$$E_M = A [j(j+1) - m^2] = AN \left[\left(v + \frac{1}{2}\right) - \frac{v^2}{N} \right], \quad (3)$$

where the label $v = j - m$ denotes the number of quanta in the oscillator. The Morse eigenstates are denoted by $[[N], v\rangle$ with $v = 0, 1, \dots, [N/2]$. The first term in E_M is the harmonic contribution, whereas the second term represents the anharmonicity which vanishes in the large N limit.

The concept of the harmonic limit provides a link with a geometrical picture, and hence can be used to compare various models of molecular structure. Here we apply this procedure for the $U(2)$ vibron model. The action of \hat{J}_μ on the Morse eigenstates is

$$\begin{aligned} \hat{J}_+ [[N], v\rangle &= \sqrt{(N-v+1)v} [[N], v-1\rangle, \\ \hat{J}_- [[N], v\rangle &= \sqrt{(N-v)(v+1)} [[N], v+1\rangle, \\ 2\hat{J}_0 [[N], v\rangle &= (N-2v) [[N], v\rangle. \end{aligned} \quad (4)$$

Next we scale the generators \hat{J}_μ appropriately and take the limit $v/N \rightarrow 0$

$$\lim_{v/N \rightarrow 0} \frac{\hat{J}_\pm}{\sqrt{N}} [[N], v\rangle = \sqrt{v} [[N], v-1\rangle \equiv a [[N], v\rangle,$$

$$\begin{aligned}
\lim_{v/N \rightarrow 0} \frac{\hat{J}_-}{\sqrt{N}} |[N], v\rangle &= \sqrt{v+1} |[N], v+1\rangle \equiv a^\dagger |[N], v\rangle . \\
\lim_{v/N \rightarrow 0} \frac{2\hat{J}_0}{N} |[N], v\rangle &= (1 - \frac{2v}{N}) |[N], v\rangle \equiv (1 - \frac{2}{N} a^\dagger a) |[N], v\rangle , \\
\frac{\hat{N}}{N} |[N], v\rangle &= |[N], v\rangle .
\end{aligned} \tag{5}$$

In the harmonic limit ($v/N \rightarrow 0$), the $U(2)$ algebra contracts to the Heisenberg-Weyl algebra which is generated by $a^\dagger a$, a^\dagger , a and 1. For example, we have

$$\frac{1}{N} [\hat{J}_+, \hat{J}_-] = \frac{1}{N} 2\hat{J}_0 \quad \rightarrow \quad [a, a^\dagger] = 1 . \tag{6}$$

The other commutation relations can be treated similarly. The application of the harmonic limit of the Morse Hamiltonian of Eq. (2) gives

$$\begin{aligned}
\lim_{N \rightarrow \infty} \frac{1}{N} \hat{H}_M &= \lim_{N \rightarrow \infty} \frac{A}{2N} (\hat{J}_- \hat{J}_+ + \hat{J}_+ \hat{J}_-) \\
&= \frac{A}{2} (a^\dagger a + a a^\dagger) = A(a^\dagger a + \frac{1}{2}) ,
\end{aligned} \tag{7}$$

with energies

$$\lim_{N \rightarrow \infty} \frac{1}{N} \hat{E}_M = A(v + \frac{1}{2}) , \tag{8}$$

in agreement with the large N limit of Eq. (3).

3 Symmetry-adapted algebraic model

The $U(2)$ model described above was introduced to treat the stretching vibrations of diatomic molecules [11]. For polyatomic molecules it was suggested to treat the vibrational excitations in terms of coupled $U(2)$ algebras. This formulation was found to be very well suited to incorporate the underlying discrete symmetries [12]. In particular, invariant interactions under the point group were constructed by applying projection techniques on an expansion of the Hamiltonian in terms of Casimir invariants. In this section, we apply this process of symmetry adaptation to the generators of the $U(2)$ algebras themselves, rather than to the Casimir operators. This procedure leads to new interaction terms.

We illustrate the method by an application to the stretching and bending vibrations of methane. In the present approach, we associate a $U(2)$ algebra with each relevant interatomic interaction. For the CH_4 molecule we have four $U(2)$ algebras corresponding to the C-H interactions and six more representing the H-H couplings. The molecular dynamical group is then given by the product $\mathcal{G} = U_1(2) \otimes \dots \otimes U_{10}(2)$, where each $U_i(2)$ algebra is generated by the set $\{\hat{G}_i\} \equiv \{\hat{N}_i, \hat{J}_{+,i}, \hat{J}_{-,i}, \hat{J}_{0,i}\}$, which satisfies the commutation relations

$$[\hat{J}_{0,i}, \hat{J}_{\pm,i}] = \pm \hat{J}_{\pm,i} , \quad [\hat{J}_{+,i}, \hat{J}_{-,i}] = 2\hat{J}_{0,i} , \quad [\hat{N}_i, \hat{J}_{\mu,i}] = 0 , \tag{9}$$

with $\mu = \pm, 0$. The labeling is such that $i = 1, \dots, 4$ correspond to the C-H couplings while the other values of i are associated with H-H interactions [20]. Here \hat{N}_i is the i -th number operator. All physical operators are expressed in terms of the generators $\{\hat{G}_i\}$, and hence commute with the number operators \hat{N}_i . For the CH₄ molecule there are two different boson numbers, N_s for the C-H couplings and N_b for the H-H couplings, which correspond to the stretching and bending modes, respectively.

The tetrahedral symmetry of methane is taken into account by projecting the local operators $\{\hat{G}_i\}$, which act on bond i , on the irreducible representations Γ of the tetrahedral group \mathcal{T}_d . For the $\hat{J}_{\mu,i}$ generators of Eq. (9) we obtain the \mathcal{T}_d tensors

$$\hat{T}_{\mu,\gamma}^{\Gamma_x} = \sum_{i=1}^{10} \alpha_{\gamma,i}^{\Gamma_x} \hat{J}_{\mu,i}, \quad (10)$$

where γ denotes the component of Γ , and the label x refers to stretching (s) or bending (b). The expansion coefficients are the same as those given in [20] for the one-phonon wave functions. The algebraic Hamiltonian is now constructed by repeated couplings of these tensors to a total symmetry A_1 .

The methane molecule has nine vibrational degrees of freedom. Four of them correspond to the fundamental stretching modes ($A_1 \oplus F_2$) and the other five to the fundamental bending modes ($E \oplus F_2$) [21]. A convenient labeling for the vibrational levels of CH₄ is provided by $(\nu_1, \nu_2^{l_2}, \nu_3^{l_3}, \nu_4^{l_4})$, where ν_1, ν_2, ν_3 and ν_4 denote the number of quanta in the $A_{1,s}, E_b, F_{2,s}$ and $F_{2,b}$ modes, respectively. The labels l_i are related to the vibrational angular momentum associated with degenerate vibrations. The allowed values are $l_i = \nu_i, \nu_i - 2, \dots, 1$ or 0 for ν_i odd or even [21]. The projected tensors of Eq. (10) correspond to ten degrees of freedom, four of which ($A_1 \oplus F_2$) are related to stretching modes and six ($A_1 \oplus E \oplus F_2$) to the bendings. Consequently we can identify the tensor $\hat{T}_{\mu,1}^{A_{1,b}}$ as the operator associated to a spurious mode. This identification makes it possible to eliminate the spurious states *exactly*. This is achieved by (i) ignoring the $\hat{T}_{\mu,1}^{A_{1,b}}$ tensor in the construction of the Hamiltonian, and (ii) diagonalizing this Hamiltonian in a symmetry-adapted basis from which the spurious mode has been removed following the procedure of [20, 22].

3.1 Zeroth order Hamiltonian

According to the above procedure, we now construct the \mathcal{T}_d invariant interactions that are at most quadratic in the generators and conserve the total number of quanta

$$\begin{aligned} \hat{\mathcal{H}}_{\Gamma_x} &= \frac{1}{2N_x} \sum_{\gamma} \left(\hat{T}_{-, \gamma}^{\Gamma_x} \hat{T}_{+, \gamma}^{\Gamma_x} + \hat{T}_{+, \gamma}^{\Gamma_x} \hat{T}_{-, \gamma}^{\Gamma_x} \right), \\ \hat{\mathcal{V}}_{\Gamma_x} &= \frac{1}{N_x} \sum_{\gamma} \hat{T}_{0, \gamma}^{\Gamma_x} \hat{T}_{0, \gamma}^{\Gamma_x}. \end{aligned} \quad (11)$$

Here $\Gamma = A_1, F_2$ for the stretching vibrations ($x = s$) and $\Gamma = E, F_2$ for the bending vibrations ($x = b$). In addition to Eq. (11), there are two stretching-bending interactions

$$\begin{aligned}\hat{\mathcal{H}}_{sb} &= \frac{1}{2\sqrt{N_s N_b}} \sum_{\gamma} \left(\hat{T}_{-, \gamma}^{F_2, s} \hat{T}_{+, \gamma}^{F_2, b} + \hat{T}_{+, \gamma}^{F_2, s} \hat{T}_{-, \gamma}^{F_2, b} \right), \\ \hat{\mathcal{V}}_{sb} &= \frac{1}{\sqrt{N_s N_b}} \sum_{\gamma} \hat{T}_{0, \gamma}^{F_2, s} \hat{T}_{0, \gamma}^{F_2, b}.\end{aligned}\quad (12)$$

The zeroth order vibrational Hamiltonian is now written as

$$\begin{aligned}\hat{H}_0 &= \omega_1 \hat{\mathcal{H}}_{A_1, s} + \omega_2 \hat{\mathcal{H}}_{E, b} + \omega_3 \hat{\mathcal{H}}_{F_2, s} + \omega_4 \hat{\mathcal{H}}_{F_2, b} + \omega_{34} \hat{\mathcal{H}}_{sb} \\ &\quad + \alpha_2 \hat{\mathcal{V}}_{E, b} + \alpha_3 \hat{\mathcal{V}}_{F_2, s} + \alpha_4 \hat{\mathcal{V}}_{F_2, b} + \alpha_{34} \hat{\mathcal{V}}_{sb}.\end{aligned}\quad (13)$$

The interaction $\hat{\mathcal{V}}_{A_1, s}$ has not been included, since the linear combination

$$\sum_{\Gamma=A_1, F_2} (\hat{\mathcal{H}}_{\Gamma, s} + \hat{\mathcal{V}}_{\Gamma, s}) = \frac{1}{4N_s} \sum_{i=1}^4 \hat{N}_i (\hat{N}_i + 2), \quad (14)$$

corresponds to the constant contribution $N_s + 2$ to the energies. Similarly, for the bending vibrations the sum of the terms

$$\sum_{\Gamma=A_1, E, F_2} (\hat{\mathcal{H}}_{\Gamma, b} + \hat{\mathcal{V}}_{\Gamma, b}) = \frac{1}{4N_b} \sum_{i=5}^{10} \hat{N}_i (\hat{N}_i + 2), \quad (15)$$

corresponds to a constant $3(N_b + 2)/2$. However, in this case the interactions $\hat{\mathcal{H}}_{A_1, b}$ and $\hat{\mathcal{V}}_{A_1, b}$ have already been excluded in order to remove the spurious contributions from the Hamiltonian.

The Hamilton of Eq. (13) is equivalent to an expansion in terms of Casimir operators. It has the advantage, though, that the spurious contributions have been eliminated from the outset. A comparison with the Hamiltonian of [20] yields three conditions on their parameters

$$\begin{aligned}A_5 + 2B_{5,10} + 8B_{5,6} &= 0, \\ B_{1,5} + B_{1,8} &= 0, \\ \lambda_{1,5} + \lambda_{1,8} &= 0.\end{aligned}\quad (16)$$

The first condition eliminates the spurious interaction from the bending Hamiltonian of [20], whereas the latter two eliminate the spurious contributions from the stretching-bending interactions. We note that the condition on the Hamiltonian that was used in [20] to exclude the spurious terms, does not automatically hold for states with higher number of quanta, nor does it remove all spurious contributions.

3.2 Harmonic limit

In the harmonic limit the interaction terms of Eq. (13) have a particularly simple form, which can be directly related to configuration space interactions

$$\lim_{N_x \rightarrow \infty} \hat{\mathcal{H}}_{\Gamma, x} = \frac{1}{2} \sum_{\gamma} (a_{\gamma}^{\Gamma, x \dagger} a_{\gamma}^{\Gamma, x} + a_{\gamma}^{\Gamma, x} a_{\gamma}^{\Gamma, x \dagger}),$$

$$\begin{aligned}
\lim_{N_x \rightarrow \infty} \hat{\mathcal{V}}_{\Gamma_x} &= 0 , \\
\lim_{N_s, N_b \rightarrow \infty} \hat{\mathcal{H}}_{sb} &= \frac{1}{2} \sum_{\gamma} \left(a_{\gamma}^{F_2, s \dagger} a_{\gamma}^{F_2, b} + a_{\gamma}^{F_2, s} a_{\gamma}^{F_2, b \dagger} \right) , \\
\lim_{N_s, N_b \rightarrow \infty} \hat{\mathcal{V}}_{sb} &= 0 .
\end{aligned} \tag{17}$$

Here the operators $a_{\gamma}^{\Gamma_x}$ are given in terms of the local boson operators a_i through the coefficients $\alpha_{\gamma, i}^{\Gamma_x}$ given in Eq. (10)

$$a_{\gamma}^{\Gamma_x} = \sum_{i=1}^{10} \alpha_{\gamma, i}^{\Gamma_x} a_i , \tag{18}$$

with a similar relation for the creation operators. From Eq. (17) the physical interpretation of the interactions is immediate. The $\hat{\mathcal{H}}_{\Gamma_x}$ terms represent the anharmonic counterpart of the harmonic interactions, while the $\hat{\mathcal{V}}_{\Gamma_x}$ terms are purely anharmonic whose contribution to the excitation energies vanishes in the harmonic limit.

We note, that the recently introduced boson-realization model [23] corresponds to the harmonic limit of the present approach, since it is formulated directly in terms of the boson creation and annihilation operators, $a_{\gamma}^{\Gamma_x, \dagger}$ and $a_{\gamma}^{\Gamma_x}$. The difference between the two lies in the anharmonic contributions which are implicit in the $U(2)$ approach, but which vanish in the harmonic limit [22].

3.3 Higher order interactions

The zeroth order Hamiltonian of Eq. (13) is not sufficient to obtain a high-quality fit of the vibrations of methane. For example, the results presented in [20] were obtained by fitting 19 vibrational energies with a r.m.s. deviation of 12.16 cm^{-1} . The boson-realization model of [23] which, as was shown above, corresponds to the harmonic limit of the present approach was applied to the same 19 vibrations with a r.m.s. deviation of 11.61 cm^{-1} . We note, however, that the latter calculation includes some higher order interactions, without significantly improving the results.

Several physically meaningful interaction terms that are essential for an improved fit are not present in Eq. (13). They arise in the present model as higher order interactions. Products of $\hat{\mathcal{H}}_i$ and $\hat{\mathcal{V}}_j$

$$\hat{\mathcal{H}}_i \hat{\mathcal{H}}_j , \quad \hat{\mathcal{V}}_i \hat{\mathcal{V}}_j , \quad \hat{\mathcal{H}}_i \hat{\mathcal{V}}_j , \tag{19}$$

are equivalent to an expansion in powers of Casimir operators. These terms only involve intermediate couplings with $\Gamma = A_1$ symmetry, since $\hat{\mathcal{H}}_i$ and $\hat{\mathcal{V}}_j$ themselves are scalars under the tetrahedral group. However, there exist other interaction terms that involve intermediate couplings with $\Gamma = A_2, F_1, E, F_2$ symmetry. For example, the interactions

$$g_{22} \hat{l}^{A_2} \hat{l}^{A_2} + g_{33} \sum_{\gamma} \hat{l}_{s, \gamma}^{F_1} \hat{l}_{s, \gamma}^{F_1} + g_{44} \sum_{\gamma} \hat{l}_{b, \gamma}^{F_1} \hat{l}_{b, \gamma}^{F_1} + g_{34} \sum_{\gamma} \hat{l}_{s, \gamma}^{F_1} \hat{l}_{b, \gamma}^{F_1} , \tag{20}$$

with

$$\begin{aligned}\hat{l}^{A_2} &= -i\sqrt{2}\frac{1}{N_b}[\hat{T}_-^{E_b} \times \hat{T}_+^{E_b}]^{A_2} , \\ \hat{l}_{x,\gamma}^{F_1} &= +i\sqrt{2}\frac{1}{N_x}[\hat{T}_-^{F_2,x} \times \hat{T}_+^{F_2,x}]_\gamma^{F_1} .\end{aligned}\quad (21)$$

split levels with the same $(\nu_1, \nu_2, \nu_3, \nu_4)$, but with different l_2 , l_3 and/or l_4 . The square brackets in Eq. (21) denote the tensor couplings under the point group \mathcal{T}_d . Similarly, all higher order terms and anharmonicities can be constructed in a systematic way. Each one of the interaction terms has a direct physical interpretation and a specific action on the various modes.

For the study of the vibrational excitations of methane we propose the following \mathcal{T}_d invariant Hamiltonian [18, 24]

$$\begin{aligned}\hat{H} &= \omega_1 \hat{\mathcal{H}}_{A_{1,s}} + \omega_2 \hat{\mathcal{H}}_{E_b} + \omega_3 \hat{\mathcal{H}}_{F_{2,s}} + \omega_4 \hat{\mathcal{H}}_{F_{2,b}} + \alpha_3 \hat{\mathcal{V}}_{F_{2,s}} \\ &+ X_{11} \left(\hat{\mathcal{H}}_{A_{1,s}} \right)^2 + X_{22} \left(\hat{\mathcal{H}}_{E_b} \right)^2 + X_{33} \left(\hat{\mathcal{H}}_{F_{2,s}} \right)^2 + X_{44} \left(\hat{\mathcal{H}}_{F_{2,b}} \right)^2 \\ &+ X_{12} \left(\hat{\mathcal{H}}_{A_{1,s}} \hat{\mathcal{H}}_{E_b} \right) + X_{14} \left(\hat{\mathcal{H}}_{A_{1,s}} \hat{\mathcal{H}}_{F_{2,b}} \right) \\ &+ X_{23} \left(\hat{\mathcal{H}}_{E_b} \hat{\mathcal{H}}_{F_{2,s}} \right) + X_{24} \left(\hat{\mathcal{H}}_{E_b} \hat{\mathcal{H}}_{F_{2,b}} \right) + X_{34} \left(\hat{\mathcal{H}}_{F_{2,s}} \hat{\mathcal{H}}_{F_{2,b}} \right) \\ &+ g_{22} \hat{l}^{A_2} \hat{l}^{A_2} + g_{33} \sum_\gamma \hat{l}_{s,\gamma}^{F_1} \hat{l}_{s,\gamma}^{F_1} + g_{44} \sum_\gamma \hat{l}_{b,\gamma}^{F_1} \hat{l}_{b,\gamma}^{F_1} + g_{34} \sum_\gamma \hat{l}_{s,\gamma}^{F_1} \hat{l}_{b,\gamma}^{F_1} \\ &+ t_{33} \hat{\mathcal{O}}_{ss} + t_{44} \hat{\mathcal{O}}_{bb} + t_{34} \hat{\mathcal{O}}_{sb} + t_{23} \hat{\mathcal{O}}_{2s} + t_{24} \hat{\mathcal{O}}_{2b} .\end{aligned}\quad (22)$$

The interpretation of the ω_i and α_3 terms follows from Eq. (17). The X_{ij} terms are quadratic in the operators $\hat{\mathcal{H}}_{\Gamma_x}$ and hence represent anharmonic vibrational interactions. The g_{ij} terms are related to the vibrational angular momenta associated with the degenerate vibrations. As mentioned above, these interactions, which are fundamental to describe molecular systems with a high degree of symmetry, are absent in previous versions of the vibron model in which the interaction terms are expressed in terms of Casimir operators and products thereof. In the harmonic limit, the expectation value of the diagonal terms in Eq. (22) leads to the familiar Dunham expansion [21]

$$\sum_i \omega_i \left(v_i + \frac{d_i}{2} \right) + \sum_{j \geq i} \sum_i X_{ij} \left(v_i + \frac{d_i}{2} \right) \left(v_j + \frac{d_j}{2} \right) + \sum_{j \geq i} \sum_i g_{ij} l_i l_j . \quad (23)$$

Here d_i is the degeneracy of the vibration. The t_{ij} terms in Eq. (22) give rise to further splittings of the vibrational levels $(\nu_1, \nu_2, \nu_3, \nu_4)$ into its possible sublevels. In the harmonic limit the t_{ij} terms have the same interpretation as in [5]. The $\hat{\mathcal{O}}_{ss}$, $\hat{\mathcal{O}}_{bb}$ and $\hat{\mathcal{O}}_{sb}$ terms give rise to a splitting of the E and F_2 vibrations belonging to the $(\nu_1, \nu_2^{l_2}, \nu_3^{l_3}, \nu_4^{l_4}) = (0, 0^0, 2^2, 0^0)$, $(0, 0^0, 0^0, 2^2)$ and $(0, 0^0, 1^1, 1^1)$ levels, respectively. Similarly, the $\hat{\mathcal{O}}_{2s}$ and $\hat{\mathcal{O}}_{2b}$ terms split the F_1 and F_2 vibrations belonging to the $(0, 1^1, 1^1, 0^0)$ and $(0, 1^1, 0^0, 1^1)$ overtones, respectively.

4 Results

The Hamiltonian of Eq. (22) involves 23 interaction strengths and the two boson numbers, N_s and N_b . The vibron number associated with the stretching vibrations is determined from the spectroscopic constants ω_e and $x_e\omega_e$ for the CH molecule to be $N_s = 43$ [20]. The vibron number for the bending vibrations, which are far more harmonic than the stretching vibrations, is taken to be $N_b = 150$. We have carried out a least-square fit to the vibrational spectrum of methane including 44 energies. We find an overall fit to the observed levels with a r.m.s. deviation which is an order of magnitude better than in previous studies. While the r.m.s. deviations of [20] and [23] are 12.16 and 11.61 cm^{-1} for 19 energies, we find a r.m.s. of 1.16 cm^{-1} for 44 energies. The values of the fitted parameters as well as all predicted levels up to $V = 3$ can be found in [18, 24].

The α_3 term plays an important role in the calculation. It is completely anharmonic in origin and its contribution to the excitation energies vanishes in the harmonic limit. In order to address the importance of this term in Eq. (22) we have carried out another calculation without this term. With one less interaction term the r.m.s. deviation increases from 1.16 to 4.48 cm^{-1} . This shows the importance of the term proportional to α_3 to obtain an accurate description of the anharmonicities that are present in the data. The absence of the α_3 term in the second calculation can only partially be compensated by the anharmonicity constants X_{ij} .

5 Summary and conclusions

In summary, we have discussed a symmetry-adapted algebraic model for molecular vibrations, in which the symmetry adaptation is applied at the level of the generators. This procedure has several interesting aspects:

- it provides a systematic procedure to construct all interaction terms up to a certain order,
- the harmonic limit gives a relation with configuration space interactions and Dunham expansions,
- the spurious states can be removed exactly.

The application to the 44 observed vibrational excitations of methane gives a good overall fit with a r.m.s. deviation of 1.16 cm^{-1} corresponding to an accuracy of $\sim 0.01 - 0.10\%$, which can be considered of spectroscopic quality.

It was pointed out that the $\mathcal{V}_{F_{2,s}}$ term in combination with the anharmonic effects in the other interaction terms plays a crucial role in obtaining a fit of this quality. Purely anharmonic terms of this sort arise naturally in the symmetry-adapted algebraic model, but vanish in the harmonic limit.

Physically, these contributions arise from the anharmonic character of the interatomic interactions, and seem to play an important role when dealing with molecular anharmonicities.

We have established an explicit relation with the algebraic model of [20], in which the Hamiltonian is expressed in terms of Casimir operators. A comparison between the two methods yields three constraints on the parameters, which remove the spurious components from the Hamiltonian of [20]. A comparison with the boson-realization model of [23] shows that this model corresponds to the harmonic limit of the present approach.

The predictability has been tested by systematically adding levels with higher number of quanta in the fitting procedure. The slow variation in the parameters shows that the model has a high degree of predictability. The application to methane [18] and to other molecules [15, 16, 17] suggest that the present model provides a numerically efficient tool to study molecular vibrations with high precision (r.m.s. deviations of $\sim 1 \text{ cm}^{-1}$).

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